ALUMINA DISPERSION STRENGTHENED COPPER-NICKEL ALLOYS

By

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Cast copper alloys containing 10, 20, and 30 percent nickel and 0.75 to 0.80 percent aluminum were machine milled into chips, then comminuted in a rod mill to fine flake powder utilizing a number of processing variables. The powders were internally oxidized, mostly at 800°C, in a low pressure oxygen atmosphere. The consolidated powders were hot extruded into bar stock. Room temperature tension tests; stress rupture tests mostly at 650°, but also at 450 and 850°C; and hardness measurements after various annealing temperature treatments to study alloy stability were performed. Excellent room temperature strength, high rupture strength at 650°C, and resistance to recrystallization at 1050°C were obtained. Problems in optimizing conditions for internal oxidation of copper-nickel base alloys are discussed.

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The interesting high temperature properties of SAP[1] have stimulated considerable effort in more refractory alloy systems where the potential for high strength alloys at high temperature is great[2-13]. A number of methods have been utilized to produce the desired fine, hard particle dispersions, of which internal oxidation[2,3,7] of dilute solid solution systems offers considerable promise by virtue of the potential for producing ultra fine, well dispersed oxides.

While most of the published works are concerned with pure metal matrices, a number of investigators have studied the effects of solid solution strengthening[10,13]. Use of more complex alloy matrices (for example, aging systems) has been unsuccessful because overaging still occurs at high temperatures in the oxide containing alloys[14,15]. Solid solution strengthening is, however, effective at very high temperatures[9,10] and might be expected to contribute importantly to the strength of oxide dispersion strengthened alloys.

For this study, internal oxidation of solid solution alloys of copper and nickel, containing small amounts of aluminum, was chosen as the method of alloy preparation.

Preparation of Alloys

Three copper alloys containing about 10, 20, and 30 percent nickel and each containing 0.75 to 0.80 percent aluminum (enough to yield about 3.5 volume percent alumina) were prepared as air cast ingots measuring 2.5 inches diameter by 6 inches high (see Table I for the analyses).

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TABLE I

Chemical Compositions of Cast Alloys
(Weight Percent)

Alloy	Nickel	Soluble Aluminum*	Residual Alumina	Copper
A3	10.16	0.76	0.024	balance
A4	20.11	0.79	0.024	balance
A5	30.07	0.80	0.037	balance

*0.8 percent aluminum produces 3.54 volume percent gamma alumina in internally oxidized alloys

Processing steps for all the alloys were as follows: (also see Table II):

1. Homogenization of the ingot at 982°C (1000°F) for 45 hours in an argon atmosphere.

2. Machine milling of ingots into fine chips. Average thickness was about 0.1 to 0.2 mm.

3. Hydrogen reduction of chips at 593°C (1100°F) for one hour to reduce copper and nickel oxides.

4. Rod milling of chips to finer powders.

5. Hydrogen treatment of powders as in step 3.

6. Internal oxidation of the powders.

7. Hydrogen treatment of oxidized powders as in step 3.

8. Hydrostatic compression of evacuated powders.

9. Sintering of compacts in hydrogen.

10. Hot extrusion.

Variations in processing among the alloys were made in steps 4, 5, and 10 (see Table II).

Table II

Summary of Steps for Alloy Production

Alloy Produced	I (1) None	II E31 (10%Ni) E51 (30%Ni)	III E41 (20%Ni)	IV E42 (20%Ni)	V E43 (20%Ni)
Process:					
Rod Milling	Air -20 + 28 mesh.	Air -400 mesh.	Alcohol and stearate, argon and hydrogen 8.5 hrs. Powder 4.6 microns thick.	Same as III except 18 hrs. Powder 3.3 microns thick.	Same as IV
Hydrogen Reduction	600°C, 1 hr.	800°C, 4 hrs. Multi-tray.	750°C, 1 hr. Boat.	620°C, 1 hr. Boat.	Same as IV
Internal Oxidation	Surf. Oxidation, 500°C. Diffuse in vacuum. 900°C, 1-12 hrs.	Oxygen from NiO. In argon. Multi-tray. 800°C, 50 hrs.	Oxygen from NiO. In argon. Rotary tube. 800°C, 5 hrs.	Oxygen from NiO blended in mix. In argon. Boat. 800°C, 5 hrs.	Same as IV except 700°C, 30 hrs.
Hydrogen Reduction	—	800°C, 1 hr. Multi-tray.	800°C, 1 hr. Rotary tube.	800°C, 1 hr. Boat.	700°C, 1 hr. Boat.
Compaction	—	Vacuum, hydrostatic, 30 Ksi.	Vacuum, hydrostatic, 6 Ksi.	Same as III	Vacuum, hydrostatic, 30 Ksi.
Sintering	—	Hydrogen, 800°C, 1 hr.	Hydrogen, 750°C, 1 hr.	Same as III	Same as III
Extrusion	(1)	Mild steel can, evacuated. 20:1 extrusion ratio, 40 in/minute, 760°C.	Same as II, except 870°C.	Same as III	Same as III, except Cu can.

(1) No alloy produced due to spinel formation.

In the past, two methods were utilized to internally oxidize alloy powders. Preston and Grant[3] surface oxidized dilute copper-aluminum powders to obtain the necessary amount of oxygen to oxidize the solute metal (aluminum and silicon), and then permitted the formed copper oxide to diffuse and react with the solute in an argon atmosphere. Bonis and Grant[4] exposed nickel-aluminum and other nickel alloys to an oxygen pressure derived from the decomposition of nickel oxide at a preselected temperature, in an argon atmosphere. Both methods are applicable and can be modified to generate a range of oxygen pressures for oxidation of the solute but not the solvent metals.

Procedure I: surface oxidation of alloy A3, Cu-10Ni-0.76Al. Powders of -20 to +28 mesh were surface oxidized at 500°C (932°F) to obtain the desired amount of oxygen for oxidation of the aluminum to alumina; the powder was then sealed in Vycor and heated at 900°C (1652°F) for various times up to 12 hours. The formed oxide was extracted by chemical solution of the powders, centrifuged, dried, weighed, and examined by X- ray diffraction using CuKα radiation.

Gamma alumina, which was expected, has the same structure as the spinel[17] $NiO.Al_2O_3$, requiring an additional check beyond X-ray analysis. A light green residue was recovered which showed the gamma alumina or spinel structure. If the spinel had formed, its amount would be based on a conversion of 1 gram of oxygen to 2.77 grams of $NiO.Al_2O_3$, whereas the same 1 gram of oxygen would yield 4.67 grams of NiO or 2.13 grams of Al_2O_3. The X-ray data, color, and weight factors clearly indicated the spinel had formed; the higher rate of agglomeration of the excess phase also indicated the spinel rather than Al_2O_3.

Accordingly surface oxidation results in too high an oxygen pressure and leads to undesired spinel formation. In all subsequent

trials, nickel oxide was selected as the oxygen source; decomposition of NiO yields a relatively low oxygen pressure which would be expected to oxidize aluminum preferentially (at 800°C the oxygen pressures over CuO and NiO are about 3.4×10^{-7} and 4.3×10^{-16} atmospheres, respectively).

Preliminary experiments with solid samples of the Cu-Ni-Al alloys were performed by exposing them to NiO at 750 and 800°C in an argon atmosphere. The depth of internal oxidation was measured as a function of time; the results are plotted in Figure 1. Also shown are the data for dilute Ni-Al (NiO source) and Cu-Al (CuO oxygen source) alloys.

It is obvious that depth of penetration of oxide in the Cu-Ni-Al alloys is very slow compared to the rates in dilute Cu-Al and Ni-Al alloys at comparable temperatures. Accordingly much finer powders were produced by milling to -400 mesh in an effort to overcome the long-time treatments which would otherwise be required.

Procedure II: oxidation of A3 and A5 powders by NiO. Hydrogen reduced chips were rod milled in air, and after every two hours of milling the -400 mesh fraction was screened out. Examination showed each particle to consist of a number of finer, welded particles, with some oxide (presumably nickel oxide) trapped internally.

Hydrogen reduction of the fine powders, internal oxidation, and again hydrogen reduction were performed with shallow powder layers (1.5 mm thick) in a multi-tray furnace arrangement. The hydrogen treatment prior to internal oxidation accomplished three tasks: surface reduction of oxides (other than Al_2O_3) formed from the milling operation, transformation of the trapped oxide to an unknown oxide (identity was not successful), and some internal oxidation of aluminum by reaction with oxygen from the trapped oxide.

Internal oxidation was for 50 hours at 800°C (1472°F) for alloys A3 and A5. Gamma alumina was identified in both alloys, and in all subsequent alloys. Figure 2a shows powder particles of A5 after internal oxidation. Weld faces are still visible in the powder agglomerates, often delineated by coarse oxides.

Procedure III: oxidation of A4 powder by NiO. In procedure III (also IV and V) rod milling was done in an inert atmosphere to minimize general oxidation, but especially to try to avoid entrapped nickel and copper oxides between welded powder particles. Ethyl alcohol and stearic acid were utilized as grinding aids[18] in a hydrogen plus argon atmosphere. For 500 grams of alloy powder, 1.8 liters of absolute ethyl alcohol and 36 grams of stearic acid were employed. Oxidation was largely minimized and no significant welding of particles was observed after 18 hours of milling. These conditions of milling lead, however, to flaking and elongation of particles; the average thickness of the powder particles was 4.6 microns after 8.5 hours and 3.3 microns after 18 hours of milling.

Internal oxidation was performed inside a rotating (one rpm) nickel tube contained in a large Vycor tube.

Extrusion (also in Proecdure IV) had to be performed at 870°C (1600°F) compared to 760°C (1400°F) for Procedure II because of unexpected extrusion press limitations for an extrusion ratio of 20:1.

Procedures IV and V: oxidation of alloy A4 in NiO. These procedures were utilized to improve on the tedious rotary tube oxidation method of Procedure III. For these compacts, 0.5 micron diameter nickel oxide in an amount just adequate to supply the oxygen necessary to oxidize the aluminum to alumina was dry blended with the milled, 3.3 microns thick copper-nickel alloy powder. This step would add

2.5 weight percent of metallic nickel after reaction, an amount not expected to materially influence the structure or properties of the final alloy; nevertheless, as a precaution, 0.025 weight percent (12.5 grams) of 0.1 micron alpha alumina powder was added to the mix to increase the Al_2O_3 content slightly. In Procedure IV, internal oxidation took place in an argon atmosphere at 800°C; in Procedure V, it took place at 700°C. Figure 2b shows a section through the flake particles of alloy A4, after internal oxidation at 800°C. Note the freedom from flake agglomeration compared to that in Figure 2a.

Results and Discussion

Figure 3 shows the microstructures, longitudinal sections, of extruded bars of the five alloys. Etching exaggerates the apparent size of the oxide particles, and serves primarily to show the tendency for oxide stringering as a result of the extrusions of the flake and elongated milled powder chips. Acid chemical extraction of the oxides, followed by X-ray line broadening measurements, indicated an average particle size for the gamma alumina of 50 to 80 angstroms; obviously the microstructural evidence is at variance with these measurements; however, at 1000X, the finest oxides are not resolvable. Coarse nickel oxides, trapped between weld-agglomerated flakes would account for some of the observed coarseness; the etching effect would account for an additional fraction of the observed coarseness.

Hardness at room temperature as a function of one hour annealing at progressively higher temperatures is a simple and useful measure of alloy stability. Figure 4 shows such hardness curves for the five alloys, and compares them to Preston and Grant's internally oxidized Cu-3.5 volume percent Al_2O_3 alloy[3], to a cold worked Cu-10 percent Ni (no oxide) alloy, and to the same alloy with 9 volume percent Al_2O_3

introduced by mechanical mixing[9].

The level of hardness values among the Cu-Ni-Al$_2$O$_3$ alloys is dependent on:

      a)   oxide content and distribution

      b)   nickel content, hardness increasing with increasing nickel

      c)   degree of cold work

      d)   recovery or recrystallization with increasing temperature.

One must keep in mind that increasing nickel content in copper increases the melting temperature; Figure 4 indicates the melting temperatures of the 0, 10, 20, and 30 percent nickel compositions as M0 to M3, respectively.

Using the Cu-3.5 volume percent Al$_2$O$_3$ alloy as a reference, this being the most temperature stable copper alloy known, one notes rather normal explainable hardness behavior among the alloys.

As nickel content increases from 10 to 30 percent, at an approximately constant Al$_2$O$_3$ content of 3.5 volume percent, hardness increases (E31, E42, E43, E51). Alloy E41 is an exception, which is expected from the very poor microstructure (Figure 3c) and the confirming poor tension test values. Alloy E43 shows the best stability, by a small fraction, over E51. Note below that these two alloys also show the highest yield and tension strength values at room temperature. The wrought Cu-10 percent Ni alloy, cold worked about 50 percent reduction of area, serves as a reference to show the increase in recrystallization resistance among the oxide stabilized alloys.

The room temperature tension test data are shown in Table III. The values appear to be related to the structures shown in Figure 3, particularly so in the case of E41. Tension and yield values for the

Table III
Room Temperature Tension Properties

Alloy	Yield, Ksi (0.2 % Offset)	Ultimate, Ksi	Elongation, %
E31	61.8	68.8	5.8
E51	72.5	81.8	6.8
E41	36.2	55.5	13.0
E42	69.6	82.2	9.0
E43	81.2	87.2	7.1
Cu - 3.5 v/o Al_2O_3[3]	65.1	76.0	13.0
Cu - 12 v/o SiO_2[3]	90.4	94.5	5.0
Cu - 10 Ni - 9 v/o Al_2O_3[9]	32.5	52.1	0.17

alloys with better structure are somewhat better than for the
Cu - 3.5 volume percent Al_2O_3 alloy, and ductility values are somewhat
poorer. If the structures of the internally oxidized Cu-Ni alloys
had been better, these values would undoubtedly have been still better.

Stress rupture tests were performed at 650°C, in air, with
spot checks at 450°C, in air, and at 850°C, in nitrogen. Results are
listed in Table IV, and are plotted for 650°C in Figures 5 and 6,
log-log plots of stress versus rupture life and versus minimum creep
rate, respectively. For comparison purposes, curves are also plotted
for the Cu - 3.5 volume percent Al_2O_3 alloy, the properties of which
are the highest reported for any copper alloy[3], for a Cu - 7.5
volume percent Al_2O_3 alloy prepared by mechanical mixing of powders;[19]
and for a wrought Cu - 10 percent Ni alloy[9]. While the Cu-Ni-Al_2O_3

Table IV
Creep-Rupture Properties

Material	Stress, Ksi	Rupt. Life, hrs.	MCR, %/hr.	Elongation, %
450°C				
E31	24.60	0.037	-	2.8
	23.00	0.271	2.3	1.5
	20.00	discontinued at 330.0 hours	nil	-
Cu-3.5 v/o Al_2O_3 (1)	40.0	75.0	-	-
Cu-7.5 v/o Al_2O_3 (2)	23.5	100.0	-	1.0
650°C				
E31	17.00	0.038	-	5.6
	15.00	1.09	1.13	4.4
	13.70	7.10	0.247	3.1
	12.20	70.8	0.0211	3.0
E51	15.00	0.173	8.33	2.4
	13.50	1.45	0.462	1.9
	12.30	12.0	0.0695	2.3
	11.00	90.6	0.0407	2.9
E41	13.50	0.092	-	7.6
	12.00	0.833	0.852	3.2
	9.00	70.73	0.0112	2.4
E42	16.50	0.015	-	2.5
	13.50	0.502	1.20	1.8
	10.00	106.2	0.00787	1.9
E31-1*	15.00	1.33	1.02	3.5
E31-2*	15.00	2.06	0.522	3.9
E51-1*	13.50	5.23	0.120	2.5
E51-2*	13.50	15.8	0.0778	2.7
E41-1*	12.00	0.51	2.31	2.6
E42-1*	13.50	3.13	0.252	3.1
E42-2*	13.50	18.55	0.0285	3.3
850°C				
E31	7.33	0.117	25.3	5.3
E42	7.33	0.106	20.0	3.6
Cu-3.5 v/o Al_2O_3 (1)	16.0	0.12	-	-

(1) Reference 3
(2) Reference 19
* See Table V for cold working and annealing treatments

alloys are not as strong as the Cu - 3.5 volume percent Al_2O_3 alloy, which showed an extremely fine, uniform particle size structure, they are as good or better than those of the Cu - 7.5 volume percent Al_2O_3 alloy prepared by mechanical mixing. The stress for a 100-hour life at 650°C for alloys E31 and E43 at about 12,000 psi is six times greater than that for the Cu - 10 percent Ni alloy without oxide.

Ductility values in all cases are low but normal for this class of alloy[3,4,10,19].

A number of investigators have shown that cold work of low oxide dispersion strengthened alloys results in improved creep rupture strength. The use of cold work with intermediate annealing treatments permits increased amounts of cold deformation with further increases in strength, accompanied not by a loss of ductility, but by a gain[10,20]. A limited number of cold swaging experiments were run with these alloys. Cold work, as well as cold work plus annealing plus further cold work treatments were performed as indicated in Table V. The test results are listed in Table IV for tests at 650°C, and the rupture life data are plotted in Figure 7.

Except for alloy E41, the first cold swaging step resulted in an increase in rupture life, accompanied by an increase in elongation. After initial swaging and testing, the balance of the alloy bars were annealed for 30 minutes at 650°C, were then further cold worked, and tested again. Rupture life increased further, accompanied by a small increase in ductility.

For a given rupture life, the cold working plus annealing treatments result in an improvement of about 2000 psi or about 20 to 30 percent increase in load carrying capacity, with an increase of 50 to 100 percent in elongation over the value for the as-extruded material.

Table V

Schedule of Cold Swaging and Annealing Treatments

Alloy	Treatment
E 31-1	E 31 cold swaged 9% reduction of area
E 31-2	E 31-1 annealed 0.5 hour at 650°C and cold swaged for total of 16.5 % reduction of area
E 51-1	E 51 cold swaged 9% reduction of area
E 51-2	E 51-1 annealed 0.5 hour at 650°C and cold swaged for total of 16.8% reduction of area
E 41-1	E 41 cold swaged 15% reduction of area
E 42-1	E 42 cold swaged 17.5% reduction of area
E 42-2	E 42-1 annealed 0.5 hour at 650°C and cold swaged for total of 32.5% reduction of area

Alloy 41, with its very poor structure, underwent extensive recovery and partial recrystallization on exposure to the 650°C test temperature after the initial cold deformation of 15 percent.

Primary concern in this study was over the lower stress rupture values obtained on internally oxidized solid solution strengthened copper-nickel alloys compared to an internally oxidized copper base alloy[3]. The oxide particle size of copper-nickel alloys was obviously coarser than for the copper - 3.5 volume percent Al_2O_3 alloy.

Three factors contributed to the poorer structures and properties of the $Cu-Ni-Al_2O_3$ alloys:

1) To obtain optimum precipitation (homogeneous) of Al_2O_3 one should have as large a supersaturation of oxygen as possible, for a given aluminum content and temperature. In conventional aging systems this is achieved by solution treating a supersaturated two-phase alloy in a single-phase field, quenching, and then aging. In internal oxidation the oxygen must be diffused into the matrix, over increasingly

long distances and is at low concentration. Further, in the case of dilute copper-aluminum alloys, the oxygen source is copper oxide; for the Cu-Ni-Al alloys the oxygen source is nickel oxide. At 800°C, the oxygen pressure in equilibrium with copper oxide is 3.4×10^{-7}, and in equilibrium with nickel oxide it is only 4.3×10^{-16} atmospheres. These two factors, plus the much lower diffusion rate of oxygen in copper-nickel alloys compared to that in copper (see Figure 1), lead to the formation of coarser Al_2O_3 particles, which coarsens further with increasing depth of oxide penetration[4,21].

2) Counter diffusion of aluminum from the center of coarser powder particles as aluminum is oxidized and depleted near the surface leads to depletion of aluminum alloy powder center. The slow diffusion of oxygen in the copper-nickel matrix further exaggerates this defect.

To estimate the severity of this problem, internally oxidized alloy powder A3 (10% Ni), which was -400 mesh material, was dissolved in dilute nitric acid in three steps (four fractions). The amount dissolved (assumed, for simplicity of calculations, to occur uniformly in each step regardless of powder size mix) was established by weighing the undissolved fraction. The Al_2O_3 in the dissolved portion was separated and weighed. The results are shown in Figure 8. It is clear that there is depletion of Al_2O_3 toward the centers of the powder particles as a result of the outward diffusion of aluminum. This effect was very much less serious in the copper-Al_2O_3 alloys, even when using considerably coarser alloy powders[3].

3) Entrapment of copper and nickel oxides between welded flakes of the alloy powders during milling of the powders.

These results, combined, lead to coarser Al_2O_3, poorer distribution and probable contamination with NiO and Cu_2O, and therefore to poorer

high temperature properties.

In view of the observed less than ideal structures it is still of importance that these Cu-Ni-Al$_2$O$_3$ alloys were stronger and more temperature stable than mebhanically mixed copper-Al$_2$O$_3$ alloys with up to 10 volume percent Al$_2$O$_3$. Further, the extreme flatness of slope of the curves in Figures 5 and 6, and the desired stability of several of these alloys to greater than 1000°C (see Figure 4) speak of the promise of these solid solution, oxide dispersion strengthened alloys for both low and high temperature use.

Conclusions

1) Alloying of copper with nickel severely slows down the rate of oxidation of aluminum in Cu-Ni-Al powdered alloys.

2) To avoid formation of nickel aluminate spinels, an oxygen pressure no greater than that in equilibrium with NiO at the same temperature may be utilized.

3) The use of low oxygen pressures in equilibrium with NiO, combined with slow diffusion of oxygen in a Cu-Ni matrix, and depletion of aluminum by counter diffusion from the centers of powder particles lead to relatively coarser Al$_2$O$_3$ particles and poorer than optimum high temperature properties.

4) In spite of these structural limitations, attractive creep rupture properties were obtained at 650°C, and structural stability was demonstrated up to 1000 or 1050°C for several of the alloys.

5) Cold work after extrusion, especially when coupled with intermediate annealing treatments, resulted in small but useful increases in high temperature strength along with an important increase in fracture ductility.

6) Solid solution alloying was primarily beneficial to the low temperature strength properties.

Acknowledgments

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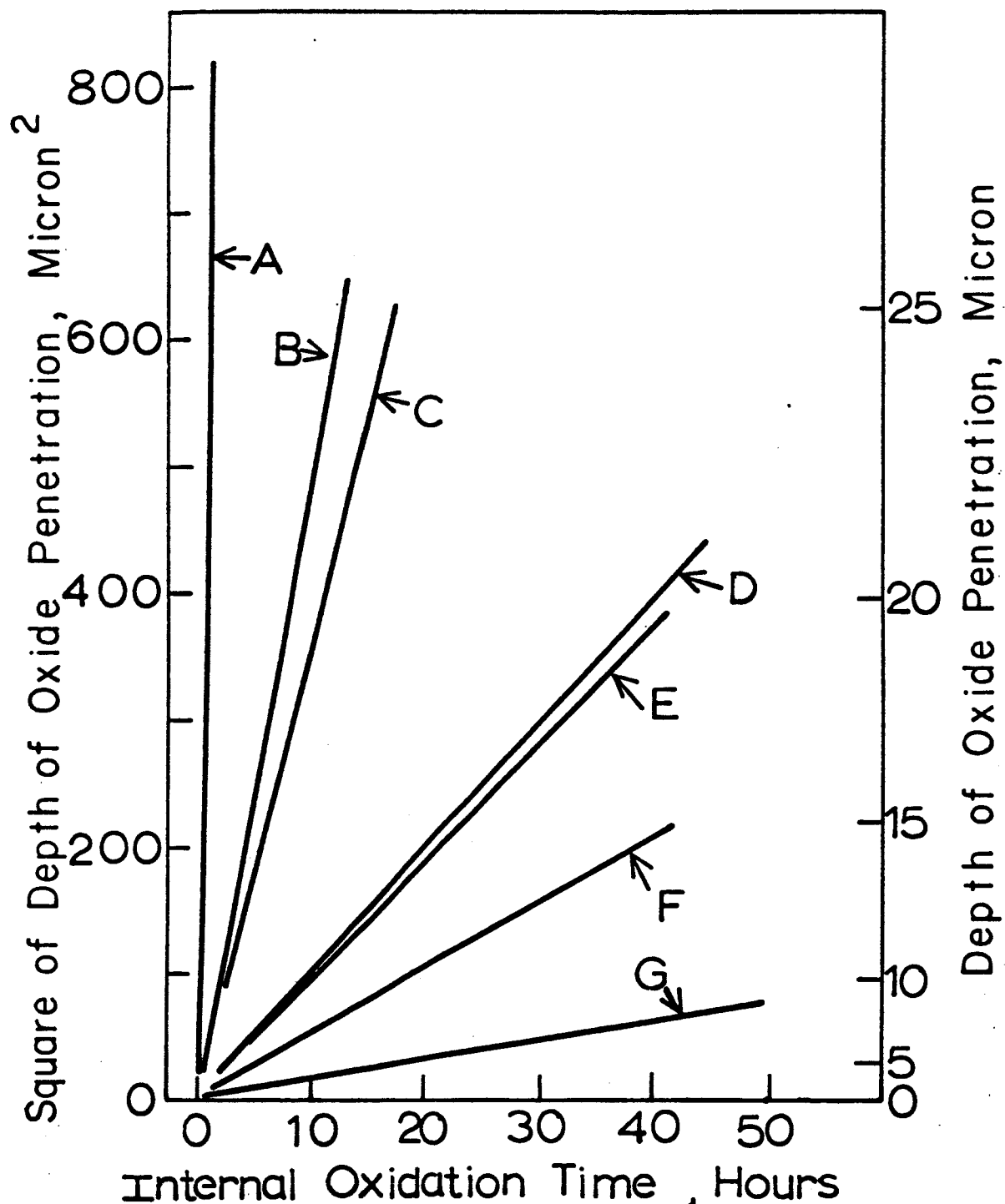
Figure 1. Depth of internal oxidation vs. time at several temperatures. Solid specimens.

A. Cu-0.72%Al, 800°C, CuO source[24]
B. Ni-0.54%Al, 800°C, NiO source[20]
C. Ni-1.43%Al, 800°C, NiO source[20]
D. A3;Cu-10Ni-0.76%Al, 800°C, NiO source
E. A4;Cu-20Ni-0.79%Al, 800°C, NiO source
F. A5;Cu-30Ni-0.80%Al, 800°C, NiO source
G. A3;Cu-10Ni-0.76%Al, 750°C, NiO source

Fig. 1

(a)

(b)

Figure 2. Sections through powders. (a) A5; Cu-30Ni-0.80%Al;
by Procedure II. Internally oxidized at 800°C for 50 hours.
(b) A4; Cu-20Ni-0.79% Al; by Procedure IV. Internally
oxidized at 800°C for 5 hours. 30% HNO_3 etch. 1000X.
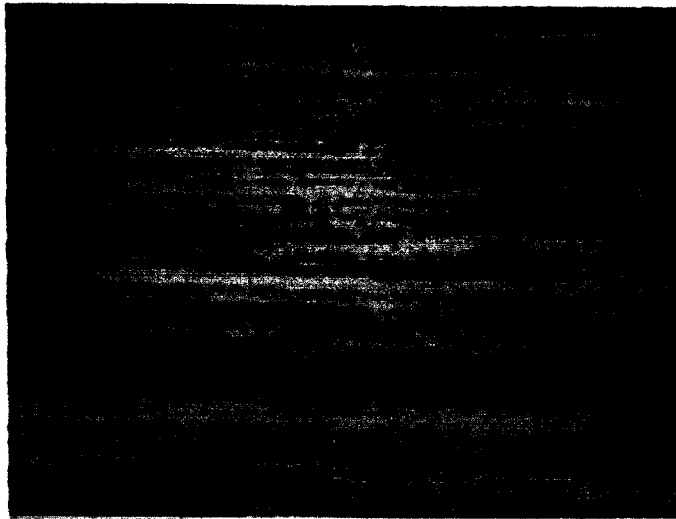
(a)

(b)

(c)

Figure 3
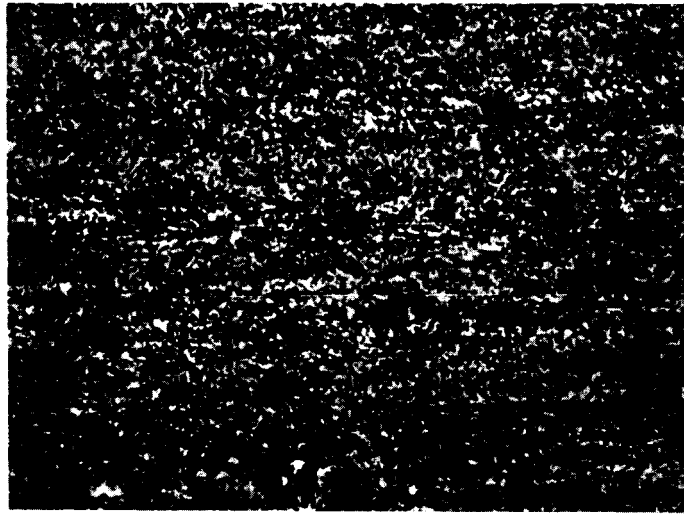
(d)
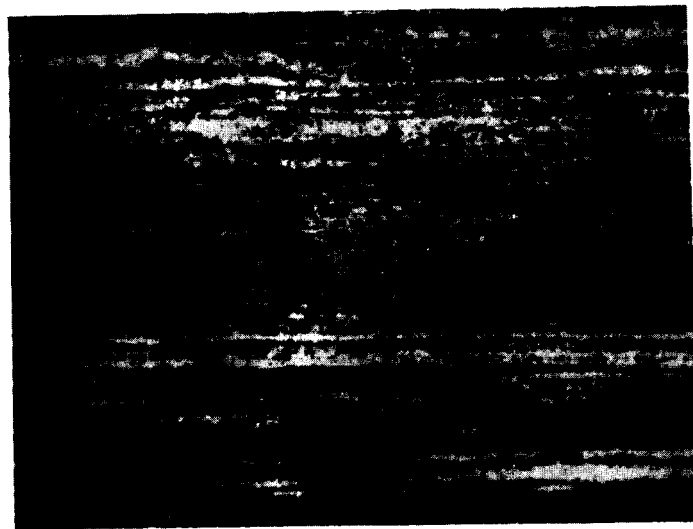
(e)

Figure 3. Longitudinal sections of as-extruded alloys. (a) E31, Procedure II. (b) E51, Procedure II. (c) E41, Procedure III. (d) E42, Procedure IV. (e) E43, Procedure V. Etched. 1000X.
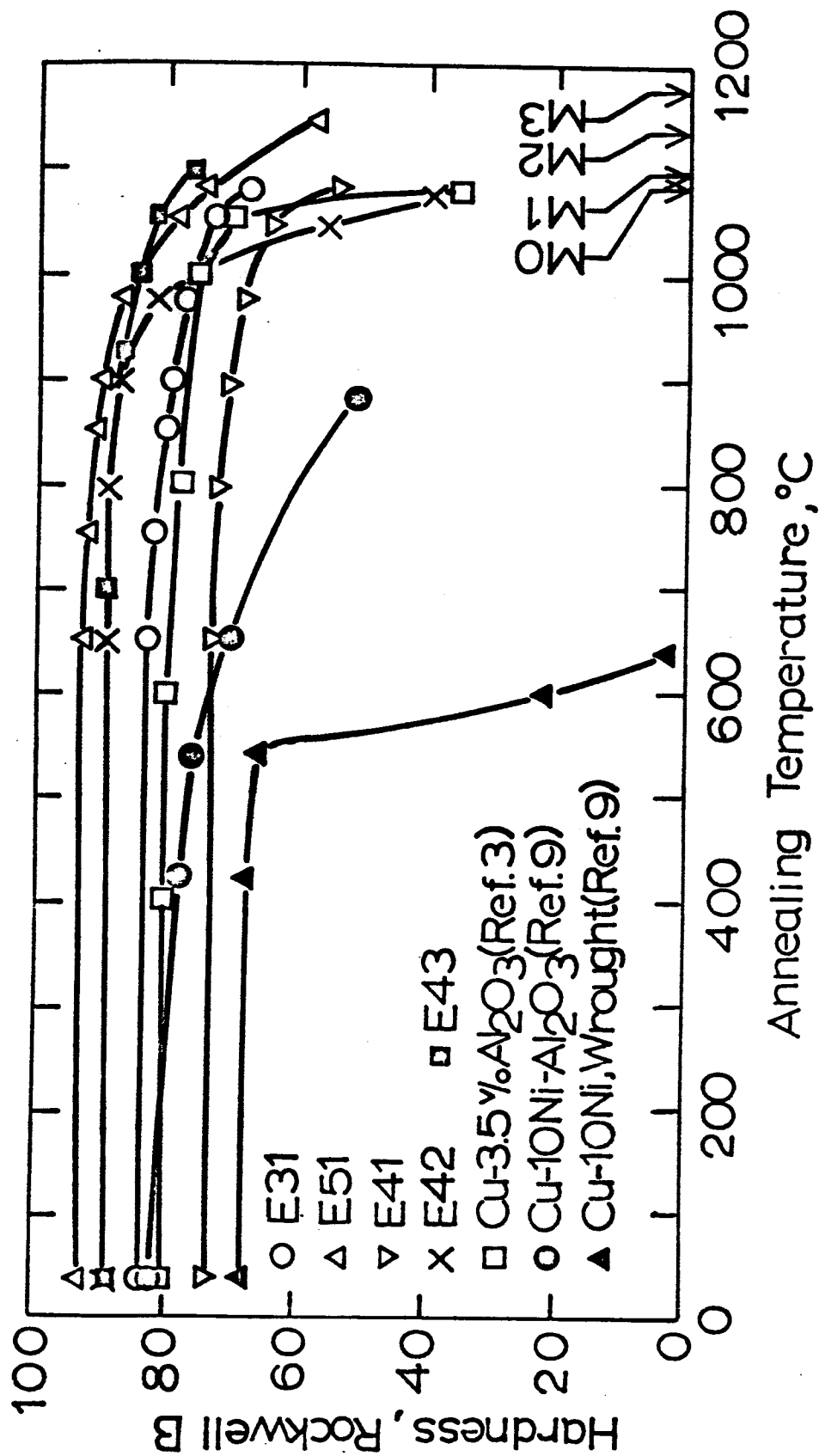
Fig. 4

Figure 4. Hardness vs. one hour annealing temperature. M0, M1, M2, and M3 are the melting temperature of pure copper, and the solidus temperatures of Cu-10Ni, Cu-20Ni, and Cu-30Ni alloys, respectively.
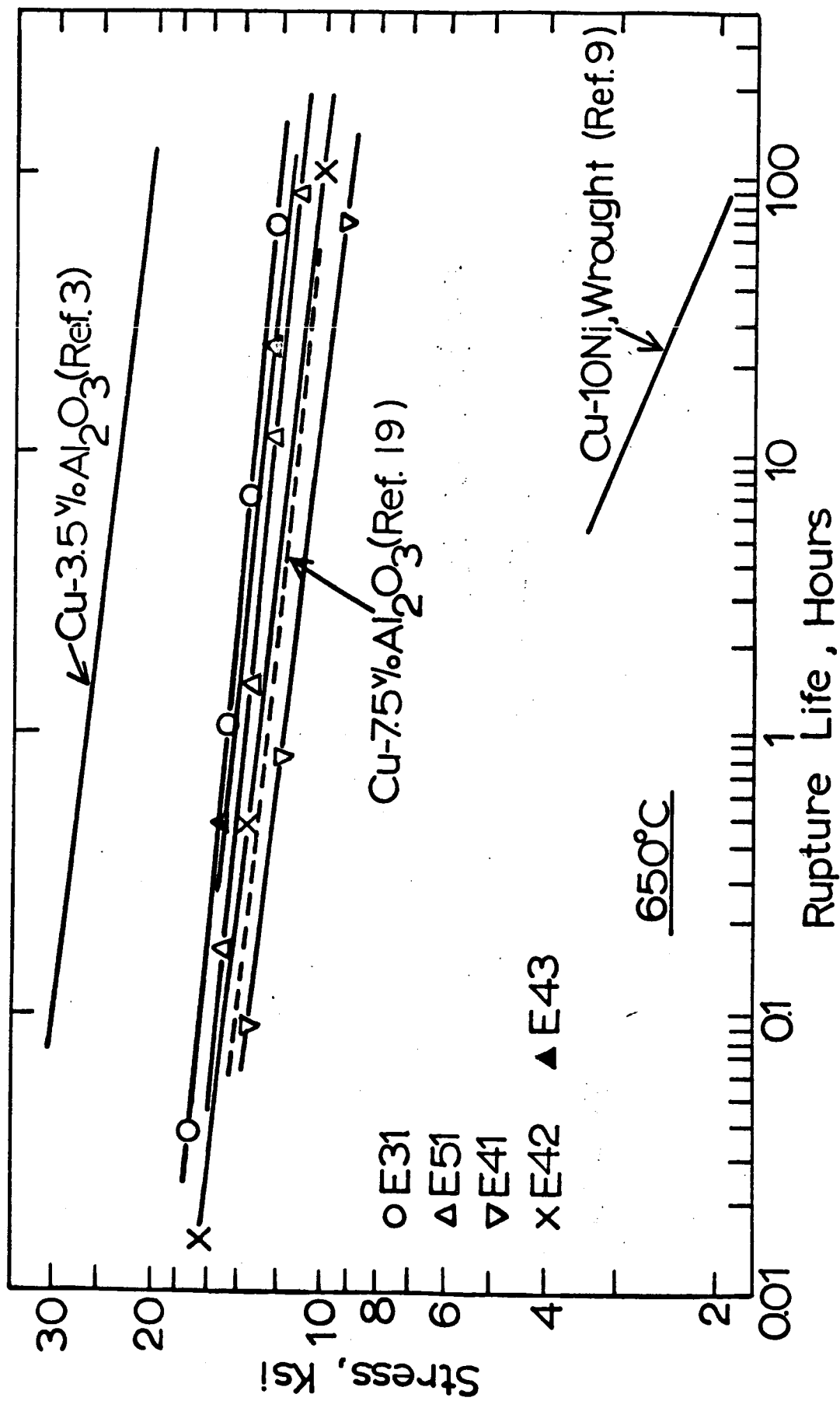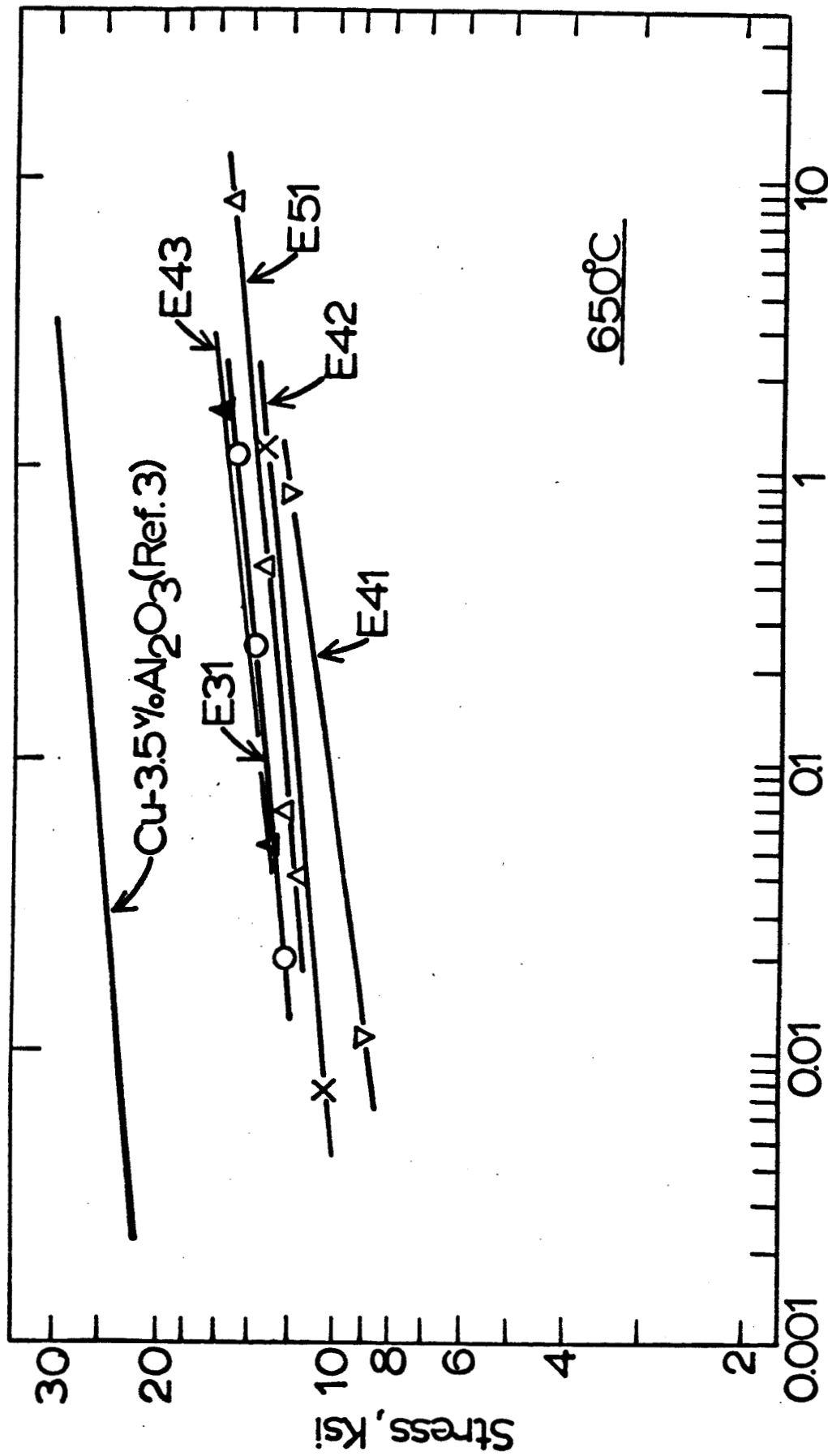
Figure 5. Log stress vs. log rupture time plot for internally oxidized Cu-Ni-Al₂O₃ allbys compared to Cu-3.5 v/o Al₂O₃ internally oxidized (3) and Cu-7.5 v/o Al₂O₃, mechanically mixed (19) and wrought Cu-10% Ni (9); all tested at 650°C.

Fig. 6

Figure 6. Log stress vs. log rupture time plot for internally oxidized Cu–Ni–Al₂O₃ alloys compared to internally oxidized Cu–3.5 v/o Al₂O₃ alloy (3); tests at 650°C.
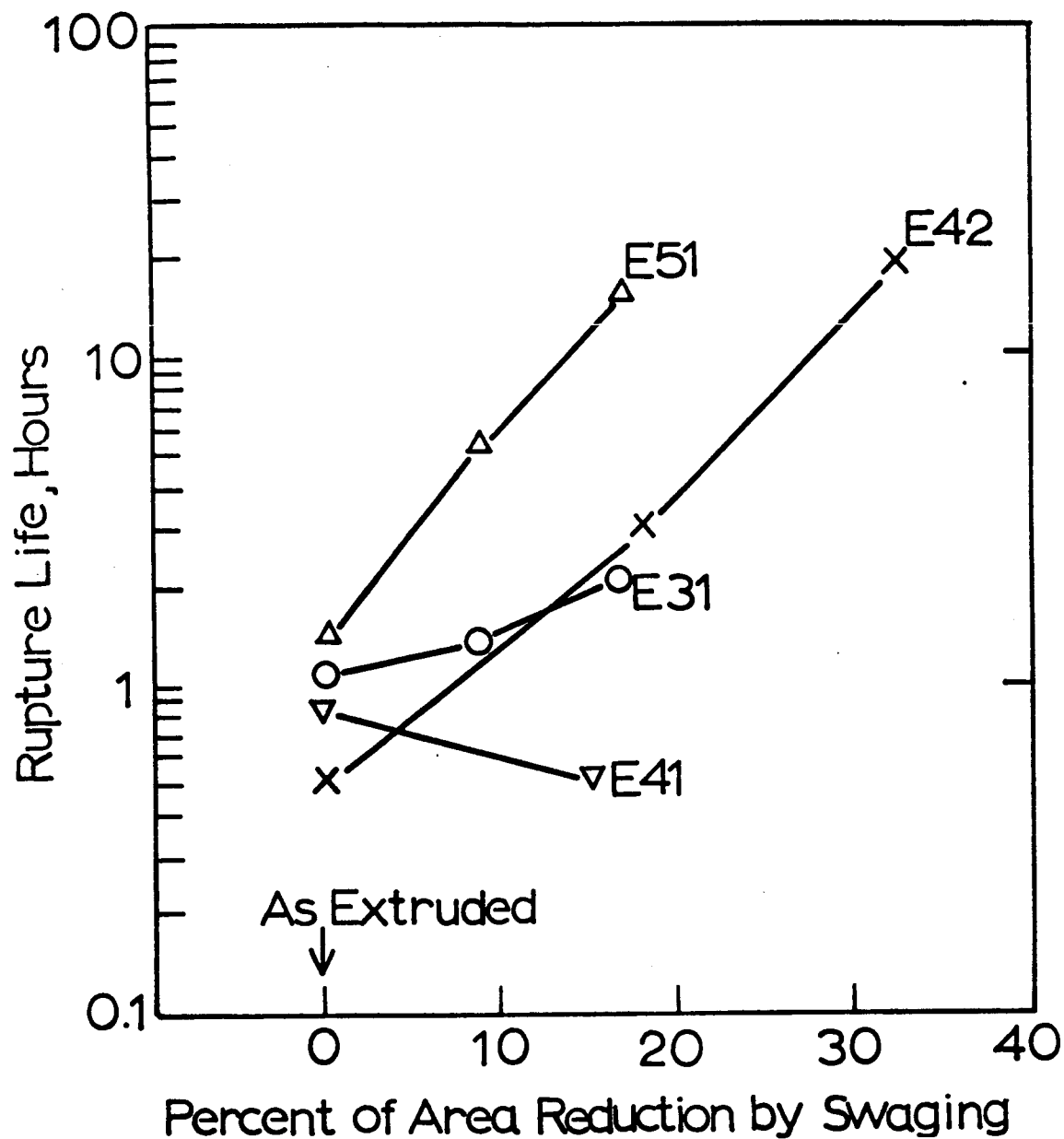
Figure 7. Effect of cold swaging and annealing on rupture life at 650°C of internally oxidized Cu-Ni-Al$_2$O$_3$ alloys. Second point is for cold work only. Third point for each alloy represents an annealing treatment, after initial cold work, of 0.05 hour at 650°C followed by further cold swaging. Stresses (Ksi) used were: E31 (15.0), E51 and E42 (13.5), E41 (12.0).
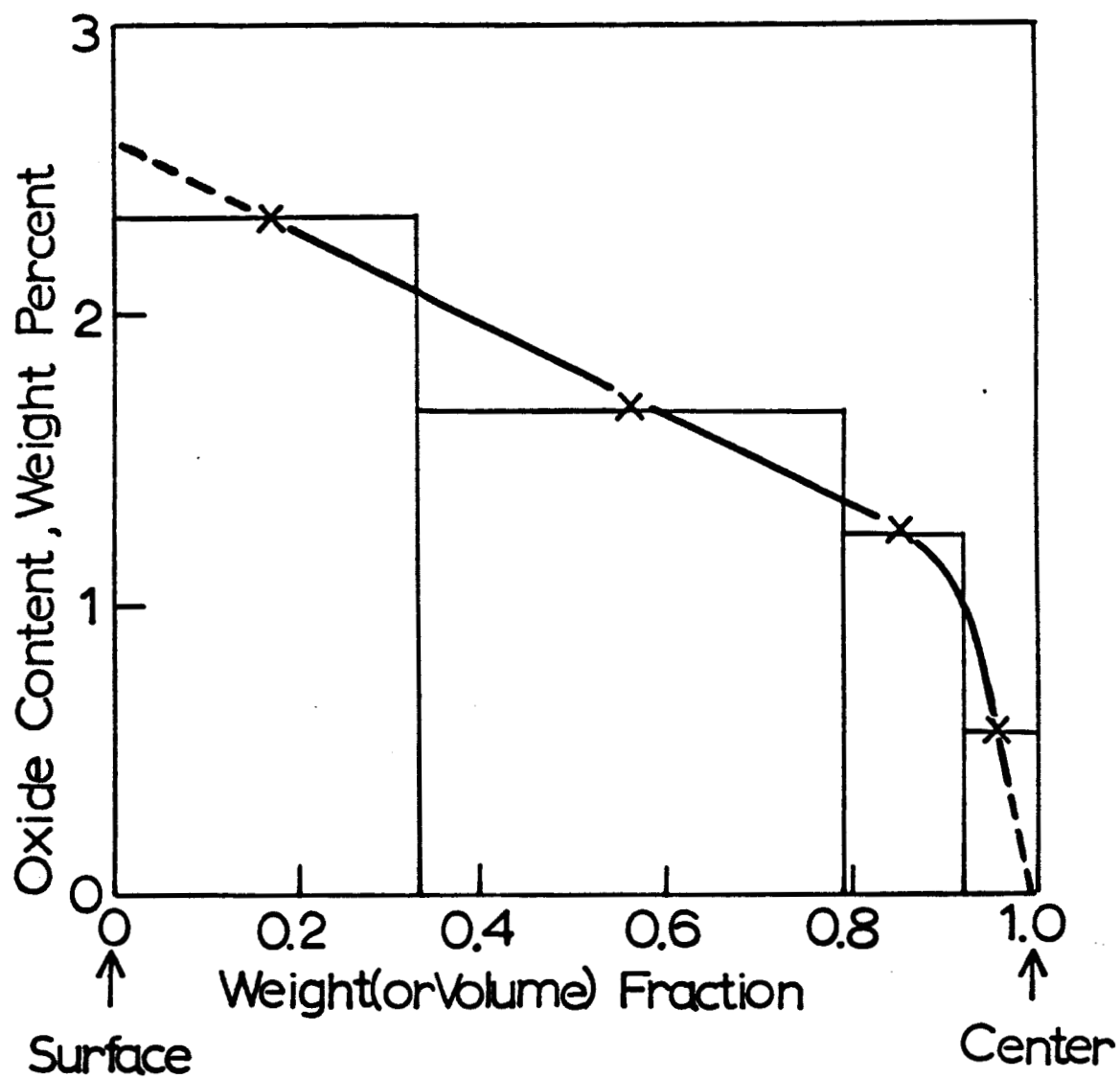
Figure 8. Aluminum oxide content as a function of depth of oxide penetration during internal oxidation. Alloy A3 (-400 mesh powder), internally oxidized at 800°C for 50 hours.